

The nature of several intense Si-H infrared stretching peaks in the neutron-transmutation-doped Si-H system

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 8519

(<http://iopscience.iop.org/0953-8984/3/44/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 10:40

Please note that [terms and conditions apply](#).

The nature of several intense Si–H infrared stretching peaks in the neutron-transmutation-doped Si–H system

L M Xie, M W Qi and J M Chen

Solid State Physics Department, Shanghai Institute of Metallurgy, Academia Sinica, Shanghai 200050, People's Republic of China

Received 1 May 1990, in final form 20 June 1991

Abstract. Our experiments show that there are four, three, two and one hydrogen atoms involved in the defect complexes corresponding to the 2210 cm^{-1} , 2066 cm^{-1} , 1980 cm^{-1} and 1832 cm^{-1} infrared (IR) peaks, respectively, in the neutron-transmutation-doped floating-zone silicon (NTD FZ-Si) system. On the basis of the correlation of the thermostability and the oscillator frequency with the number of hydrogen atoms involved in these IR peaks, we attribute the 2210 cm^{-1} , 2066 cm^{-1} , 1980 cm^{-1} and 1832 cm^{-1} IR peaks to the vacancy+4H, vacancy+3H, vacancy+2H and vacancy+1H defect complexes, respectively. The mechanism of the formation of the vacancy+ n H defect complexes in the NTD FZ-Si:H system has been discussed.

1. Introduction

Since numerous hydrogen-related infrared (IR) absorption peaks in the proton-implanted crystalline silicon (c-Si) were first observed by Stein [1], much interest has also arisen in floating-zone silicon (FZ-Si) containing hydrogen [2–9]. Hydrogen can be introduced into silicon during crystal growth in a hydrogen atmosphere. It is well known that hydrogen saturates the dangling bond at the location of defects in c-Si and gives rise to local vibrational modes and corresponding Si–H IR peaks. The radiation defects introduced by the neutron irradiation and the defect interaction with the hydrogen already present in c-Si produces various H defect complexes, which makes the IR spectra in neutron-transmutation-doped (NTD) FZ-Si:H system more complicated [10]. Because all Si–H IR peaks have different annealing characteristics, therefore they must correspond to discrete Si–H vibration centres. Although much work has been done both experimentally and theoretically [11–14], owing to the limited experimental information there is lack of common understanding about the nature of the Si–H IR absorption peaks in the NTD FZ-Si:H system. Clarifying these peaks could help us to understand the nature of the H defect complexes and their relation.

In this paper, we report some experimental results on intense Si–H IR stretching peaks observed in the neutron-irradiated FZ-Si:H system, which verify that the vacancy + n H ($V + nH$) ($n = 1-4$) complexes are present in the NTD FZ-Si:H system.

2. Experimental details

The FZ-Si crystal, of $\langle 111 \rangle$ crystal orientation and resistivity $\rho > 400\ \Omega\text{ cm}$, were grown in a hydrogen or deuterium (D) atmosphere or in H + D (36% H–64% D) with the same

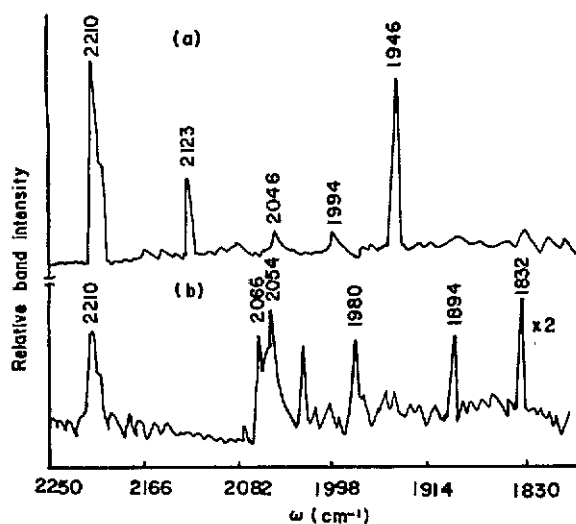


Figure 1. The room-temperature IR spectra of the FZ-Si:H in the stretching region: (a) in the as-grown state; (b) after neutron radiation at a dose of 10^{18} neutrons cm^{-2} .

technology in the same furnace. The FZ-SiH(D) systems were all of n type, with oxygen content less than $5 \times 10^{16} \text{ cm}^{-3}$, carbon content less than $1 \times 10^{16} \text{ cm}^{-3}$, and other impurities less than $5 \times 10^{14} \text{ cm}^{-3}$. All the samples were cut to a thickness of about 5 mm and mechanically polished to a mirror surface on both sides before irradiation. The samples were subjected to neutron irradiation in the light-water nuclear reactor. The total irradiation dose ranged from 10^{15} to 3.7×10^{18} neutron cm^{-2} . During irradiation, a sample temperature of about 40°C was maintained. The cadmium ratio was 10:1. After irradiation, the sample underwent annealing at different temperatures between 100 and 600°C in a flowing pure nitrogen atmosphere. The annealing temperature was held constant for 30 min. After annealing, the oxide layer of the samples was removed by hydrofluoric acid. A NiC-7199C Fourier transform infrared (FTIR) spectrometer was used. A high-purity vacuum FZ-Si sample with the same thickness was used as a reference. The effect of moisture was compensated by subtracting the IR spectrum of the air from that of the reference sample. An Air Products closed-cycle cooling system was used for low-temperature (10 K) experiments.

3. Results and discussion

Typical spectra of the FZ-Si:H system in both the as-grown state and the post-neutron irradiation state in the stretching vibration region of the Si-H bond are presented in figures 1(a) and 1(b). It can be seen from figure 1(a) that there are two intense Si-H IR peaks—2210 (2223) and 1946 (1952) cm^{-1} —and some minor peaks between them in the as-grown state. Here the wavenumbers in parentheses are the positions of the corresponding absorption peaks at 10 K; both of them denote the same Si-H IR peak. More extra pronounced Si-H IR peaks observed in the irradiated samples as shown in figure 1(b) are located at 2066 (2072, 2068), 1980 (1990, 1987), 1894 (1910) and 1832 (1839) cm^{-1} .

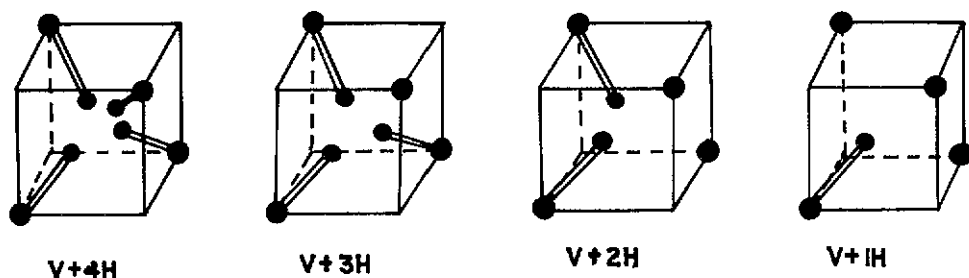


Figure 2. The configuration for V + 4H ($n = 1-4$). The larger full circles represent Si and the smaller ones H.

Table I. The stretching vibration modes of the V + n H defect complexes.

| Configuration | Vibration modes |
|---------------|-----------------|
| V + 4H | $A_1^a + T_2$ |
| V + 3H | $E + A_1$ |
| V + 2H | $A_1 + B_2$ |
| V + 1H | A_1 |

^a IR inactive.

The configurations for V + n H ($n = 1-4$) are shown in figure 2. From figure 2, we can use the group theory [15] to analyse the stretching vibrational modes for V + n H ($n = 1-4$). From the calculated results with a valence force field and the table of the correlation of the group to its subgroups, it is known that the symmetry stretching vibrations of V + n H ($n = 1-4$) are all developed from the A_1 mode, the asymmetry stretching vibrations of V + n H ($n = 1-4$) came from the T_2 , E and B_2 modes. Table 1 summarizes the stretching vibrational modes for V + n H ($n = 1-4$). It can be seen from table 1 that in the case of the 4H configuration the A_1 mode is IR inactive, and the oscillator strength is equal to zero, while the T_2 mode is IR active. With a decrease in the number of hydrogen atoms in the configuration, the symmetry is lower and the A_1 mode became IR active. According to the following experimental evidence, we expect the 2210, 2066, 1980 and 1832 cm^{-1} intense IR peaks in the NTD FZ-Si:H system to correspond to V + n H ($n = 1-4$) defect complexes.

3.1. The fine structure

3.1.1. 2210 (2223) cm^{-1} peak. The major peak in the as-grown FZ-Si:H system at 2210 cm^{-1} is believed to be the complex involving H and native lattice defects. In the case of neutron irradiation, the intensity of the 2210 cm^{-1} peak decreases with dose increase. The 2210 cm^{-1} peak is the most stable and anneals out at 550 °C.

We have obtained some significant results [7] on the 2210 cm^{-1} peak with the help of the isotope effect of hydrogen and 10 K measurement. At 10 K, the peak splits into three

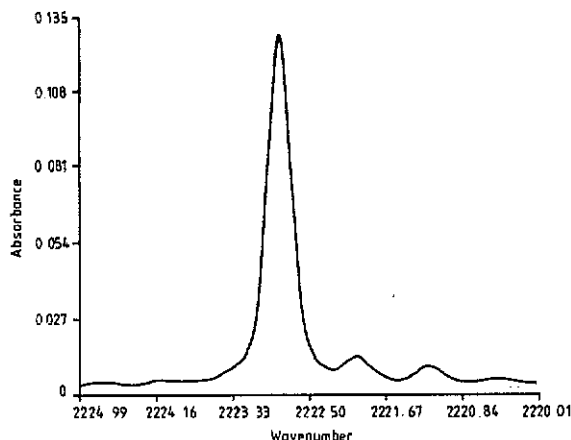


Figure 3. The 2210 cm^{-1} peak splitting at 10 K due to the Si isotope effect.

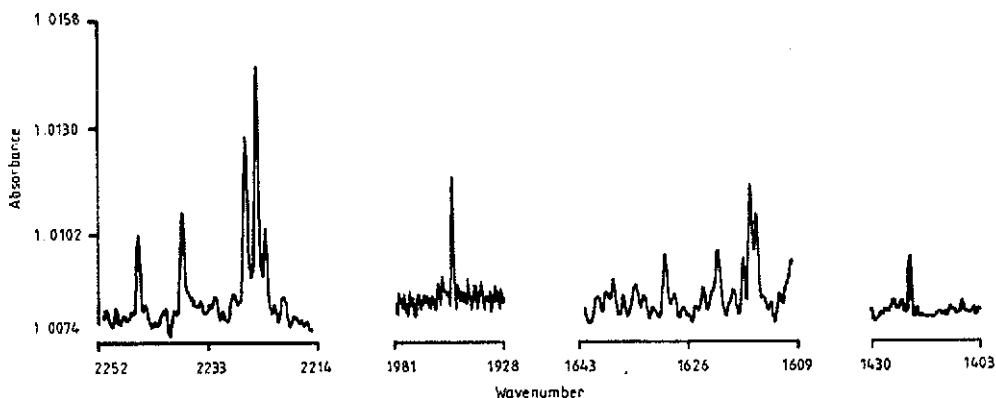
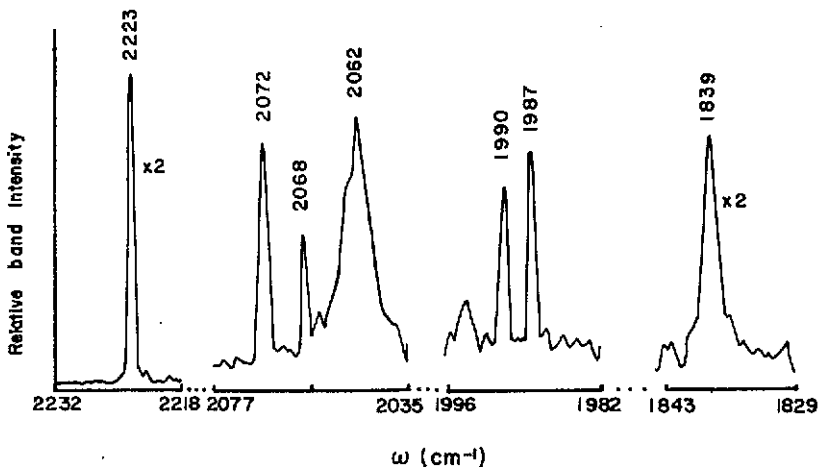


Figure 4. The low-temperature (10 K) IR spectrum of the FZ-Si: 36% H-64% D in the stretching region.

peaks: (2223) , (2222) and $(2221)\text{ cm}^{-1}$. As shown in figure 3, the ratios of the intensity of these three peaks are proportional to the natural abundance of Si isotopes (^{28}Si , ^{29}Si and ^{30}Si). Obviously, it is not related to the impurities except for hydrogen. When hydrogen is replaced by deuterium, the $(2223)\text{ cm}^{-1}$ peak shifts to $(1617)\text{ cm}^{-1}$ in accordance with the increase in the reduced mass due to isotope substitution. The (2223) and $(1617)\text{ cm}^{-1}$ peaks split further into five peaks during partial substitution of deuterium for hydrogen (36% H-64% D). As shown in figure 4, there is a corresponding one-to-one relationship between the (2245) , (2237) , (2226) , (2224) and $(2223)\text{ cm}^{-1}$ in the Si-H stretching vibration region and the (1629) , (1621) , (1615) , (1613) and $(1617)\text{ cm}^{-1}$ peaks in the Si-D stretching vibration region. Because the symmetry of the defect complex in c-Si cannot exceed the point group symmetry of the silicon lattice, e.g. T_d , so the complex corresponding to the 2210 cm^{-1} peak should be of T_d . When some of the hydrogen atoms in the defect complex are replaced by deuterium, the symmetry of the complex is lowered, so that the IR-inactive A_1 mode became IR active and the triply

Table 2. The configurations of the complex corresponding to the 2210 cm^{-1} peak in the FZ-Si:H + D sample, their symmetry and IR-active modes.

| Configuration | Symmetry | Stretching vibration modes |
|---------------|----------|--|
| 3H1D(1H3D) | C_{3v} | E |
| 4H(4D) | T_d | T_2 (splits into A_1 , $(A_1)^a$, B_1 , B_2) |
| 2H2D | C_{2v} | B_2 , B_1 , A_1 |

^a IR inactive.**Figure 5.** The IR spectrum of NTD FZ-Si:H at 10 K. Only the interesting regions are shown to indicate the fine structure of the 2066 and 1980 cm^{-1} IR peaks.

degenerated T_2 mode splits into modes of lower degree of degeneracy, thus leading to the series of new IR absorption peaks. According to the number of hydrogen and deuterium atoms in the complex, there are five different configurations 4H, 3H1D, 2H2D, 1H3D and 4D in the FZ-Si:H + D system. Table 2 shows the symmetry of each configuration and the number of IR-active modes contributed by them. Thus the group theory analysis of this result leads to the conclusion that the complex responsible for the 2210 cm^{-1} peak contains four hydrogen atoms and has T_d symmetry.

The valence force calculation of the oscillator frequencies [11], semi-empirical minimum neglect of diatomic overlap (MNDO) calculation [12] and the quantitative explanation of the anomalous temperature effect of the linewidth at 200 K [13, 14] demonstrate that the V + 4H defect complex is responsible for the 2210 cm^{-1} peak.

3.1.2. 2066 (2068, 2072) cm^{-1} peak. Figure 5 shows the (2068) and (2072) cm^{-1} peaks are split from the room-temperature peak at 2066 cm^{-1} . They appear only in the NTD FZ-Si:H system [5, 10]. The dependence of the IR absorption coefficients α of the two

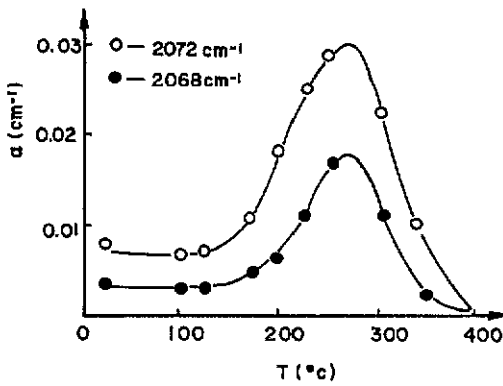


Figure 6. The dependence of the IR absorption coefficient α of the 2072 and 2068 cm^{-1} IR peaks on annealing temperature.

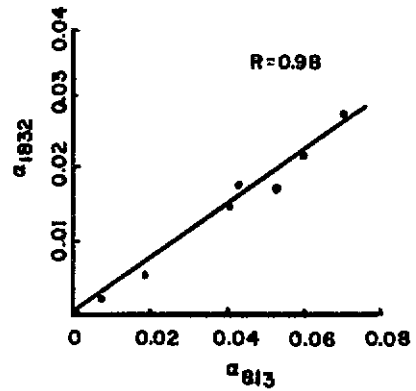


Figure 7. The correlation between the 1832 cm^{-1} peak and the bending mode 813 cm^{-1} .

peaks on the annealing temperature is shown in figure 6. With the correlation coefficient $R = 0.95$, this means that the (2072) and (2068) cm^{-1} peaks arise from the same vibration centre. They disappear on annealing at 400 $^{\circ}\text{C}$. Another characteristic is that the intensity of the (2072) cm^{-1} peak is approximately twice that of the (2068) cm^{-1} peak. A credible explanation is that the (2072) and (2068) cm^{-1} peaks are responsible for the E mode (twofold) and the A_1 mode (onefold), respectively, as shown in table 1. The point group of the 2066 cm^{-1} peak is C_{3v} and its configuration is as shown in figure 2. Thus we can say that there are three hydrogen atoms involved in the defect complex corresponding to the 2066 cm^{-1} peak. The investigation of the absorption coefficient a of the 2066 cm^{-1} peak versus the neutron irradiation doses show that the 2066 cm^{-1} peak comes from $V + 4H$, in which one of the SiH bonds is broken by the radiation effect of the neutrons; we discuss this issue later. Therefore, the $V + 3H$ defect complex is responsible for the 2066 cm^{-1} peak.

3.1.3. 1980 (1987, 1990) cm^{-1} peak. The 1980 cm^{-1} peak splits into two correlated peaks at (1987) and (1990) cm^{-1} at 10 K as shown in figure 5. These two peaks were found to both have the same production and annealing behaviour with a correlation coefficient $R = 0.89$. This result is consistent with the case of electron irradiation [16]; it seems that they arise from the same vibration centre. This result also indicates that the centre contains two hydrogen atoms, which can vibrate symmetrically and asymmetrically. The (1987) and (1990) cm^{-1} peaks are responsible for the A_1 mode and B_1 mode, respectively, as shown in table 1. The point group of the 1980 cm^{-1} peak is C_{2v} and its configuration is as shown in figure 2. It is naturally thought that the major radiation-induced SiH IR peaks may be of the simple H-vacancy type of defect complex, because the 1980 cm^{-1} peak also appears in the case of γ -ray [17] and electron [16] irradiation. Therefore, the $V + 2H$ defect complex might be responsible for the 1980 cm^{-1} IR peak. The same model, named the Z centre, has been proposed by Du *et al* [8] to explain a DLTS level ($E_c = 0.2 \text{ eV}$) discovered in the NTD FZ-Si:H system, which has a similar annealing behaviour as the 1980 cm^{-1} peak in our experiment.

3.1.4. 1832 (1839) cm^{-1} peak. The most common and pronounced peak, whether γ -ray [17], electron [16], neutron [5, 10] or proton [1, 18] irradiation is used at 1832 cm^{-1} . The

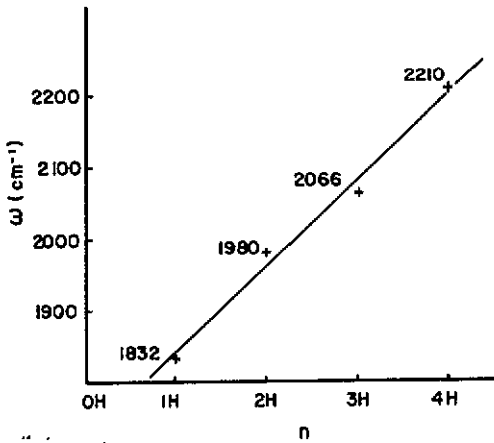


Figure 8. The correlation of the oscillator frequencies with the number of H atoms contained in the 2210, 2066, 1980 and 1832 cm^{-1} IR peaks.

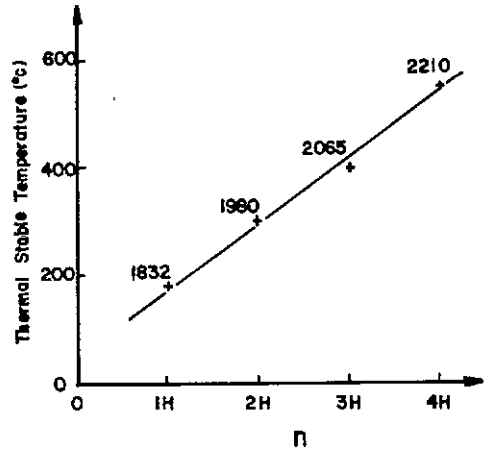


Figure 9. The correlation of the thermal stability temperature with the number of H atoms contained in the 2210, 2066, 1980 and 1832 cm^{-1} IR peaks.

1832 cm^{-1} peak does not split at 10 K but is closely associated with the 813 (817) cm^{-1} peak in the bending vibration region with the correlation $R = 0.98$ as shown in figure 7, indicating that they belong to the same vibration centre. In the NTD FZ-Si:D system, the 1832 cm^{-1} peak shifts to (1339) cm^{-1} while, in the sample containing both H and D, the (1839) and (1339) cm^{-1} peaks do not show any splitting even at 10 K. The 1832 cm^{-1} peak has the lowest annealing temperature (175 °C) and lowest vibration frequency of the Si-H IR stretching vibration peaks in the FZ-Si:H system [19]. From these results, one can conclude that the 1832 cm^{-1} peak is due to a simple vacancy type of defect complex containing one hydrogen atom, so that the 1832 cm^{-1} peak is responsible for the A_1 mode of V + 1H complex.

To summarize the above, there are four, three, two and one hydrogen atoms involved in the H defect complexes corresponding to the 2210 cm^{-1} , 2066 cm^{-1} , 1980 cm^{-1} and 1832 cm^{-1} peaks, respectively. This agrees with our proposal that they correspond to the V + 4H, V + 3H, V + 2H and V + 1H defect complexes.

3.2. The relationship between the vibration frequency of IR peaks and the number of H atoms contained

The basic property of the V + 4H model is characterized by the fact that the four hydrogen atoms repel each other [11]. This is because the repulsive interaction of the H-H non-bonded atoms increase the stretching vibrational force constant of the Si-H bond. The vibrational potential functions calculated by MNDO [12] show that the force constants of the vibration frequencies of the V + nH defect complexes increase with the increasing number of hydrogen atoms. This means that the position of the vibration frequencies of the IR absorption peaks caused by the V + nH defect complexes appear in the IR spectra is in the order of the number of hydrogen atoms which the IR peaks contained. The vibration frequencies of the IR peaks versus the number of hydrogen atoms contained is shown in figure 8. The experimental result indicates that the vibration

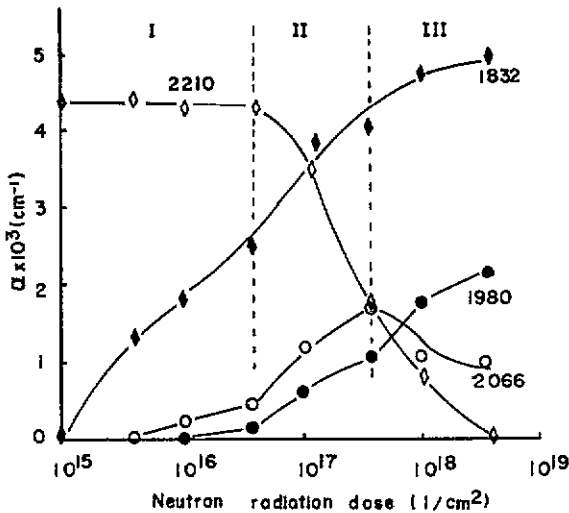


Figure 10. The absorption coefficient α of the 2210, 2066, 1980 and 1832 cm^{-1} IR peaks versus the neutron irradiation doses for FZ-Si:H.

frequencies of the IR peaks increase with the increasing number of hydrogen atoms contained, which quite agrees with our analysis above. The linear behaviour means that the force constant of the 2210, 2066, 1980 and 1832 cm^{-1} peaks are equal to $f_0 + n \Delta f = 1.75 + 0.24 n \text{ dyn } \text{Å}^{-1}$ (where $\omega = \{[f_0 + n \Delta f]/m\}^{1/2} = \omega_0 + n \Delta f/2\omega_0 m$), which coincides with the MNDO [12] calculation. The decrease in the number of hydrogen atoms in $V + nH$ causes a reduction in the van der Waals repulsion force between hydrogen atoms. This effect results in a shift of the vibration mode to a lower frequency.

3.3. The relationship between the thermal stability of the IR peaks and the number of hydrogen atoms contained

The vacancy in silicon is unstable and the activation energy of diffusion for a vacancy (0.3 eV) in c-Si is small; so it can migrate through the Si lattice at the liquid-nitrogen temperature. Likewise the hydrogen atom in c-Si has a low diffusion energy (0.48 eV) and can move easily at room temperature. However, when these two species bond together, the situation is entirely different. In c-Si, the Si-H bond energy is about 2–3 eV [20]. It is obvious that the total energy of the $V + nH$ defect complex should be reduced and its thermal stability must increase with increasing number of hydrogen atoms attaching to the dangling bonds of the vacancy. Here, by thermal stability we mean the annealing-out temperature for the IR peaks. Figure 9 shows the annealing-out temperature of the 2210, 2066, 1980 and 1832 cm^{-1} peaks versus the number of hydrogen atoms contained in the corresponding defect complexes. The experimental result is quite consistent with attributing the 2210 cm^{-1} , 2066 cm^{-1} , 1980 cm^{-1} and 1832 cm^{-1} peaks to $V + 4H$, $V + 3H$, $V + 2H$ and $V + 1H$, respectively.

3.4. The formation of the defect complexes of $V + nH$ in the NTD FZ-Si:H system

Figure 10 represents the absorption coefficients α of 2210, 2066, 1980 and 1832 cm^{-1} peaks versus the neutron irradiation doses for the FZ-Si:H system. Obviously, there are three regions separated by the two vertical broken lines in the figure. The fact that the intensities of the radiation-induced 2066, 1980 and 1832 cm^{-1} peaks increase with

Table 3. The summary of the assignment, configuration and vibration modes corresponding to 2210, 2066, 1980 and 1832 cm^{-1} IR peaks in NTD Si:H system.

| Peak position (cm^{-1}) | Configuration | Vibration modes |
|------------------------------------|---------------|-----------------|
| 2210 (2223) | V + 4H | T_2 |
| 2066 (2072, 2068) | V + 3H | $E + A_1$ |
| 1980 (1990, 1987) | V + 2H | $A_1 + B_2$ |
| 1832 (1839) | V + 1H | A_1 |

increasing neutron radiation dose while the intensity of the 2210 cm^{-1} peak for the as-grown state remains unchanged in the same dose range 10^{15} – 10^{16} neutrons cm^{-2} indicates their relation with the radiation-induced defect complexes. Moreover, the hydrogen incorporated into the radiation-induced defect complexes does not come from the original defect complexes but from the hydrogen which is dissolved in the c-Si or is IR inactive, most probably from hydrogen molecules located in the T_d interstitial site as predicted theoretically before [20]. The intensity of the 2210 cm^{-1} peak starts to decrease monotonically as the neutron irradiation dose exceeds 5×10^{16} neutrons cm^{-2} , while the slope of the intensity versus radiation dose of the other three IR peaks become steeper. A reasonable explanation of this phenomenon is that V + 4H defect complexes, in which one or more Si-H bonds are broken by the radiation effect of neutrons, are transformed into V + 3H, V + 2H and V + 1H defect complexes. For a similar reason, further intense neutron irradiation may cause the V + 3H defect complex to transform into V + 2H and V + 1H defect complexes. A clue to this behaviour can be found in the third region in figure 10. On studying once again the previous results on the electron-irradiated FZ-Si:H system, we can see that the fact that the 2066 cm^{-1} peak does not exist matches with the fact that the as-grown Si-H band 2210 cm^{-1} remains unchanged after electron irradiation in the dose range 5×10^{15} – 1×10^{17} electrons cm^{-2} [16]. This experimental result can be considered to arise because there is only a small possibility that three H atoms enter the same Si vacancy to form a V + 3H defect complex. Therefore, the IR-detectable 2066 cm^{-1} peak comes from the fragmentation of V + 4H, which naturally explains why the 2066 cm^{-1} peak is only present in the NTD FZ-Si:H system.

4. Conclusion

(1) The fine structure of the IR spectra at low temperatures, the isotopic effect and the correlation between IR peaks in the NTD FZ-Si:H system indicate that there are four, three, two and one hydrogen atoms involved in the vacancy-type defect complexes corresponding to the 2210 cm^{-1} , 2066 cm^{-1} , 1980 cm^{-1} and 1832 cm^{-1} peaks, respectively, in the NTD Si:H system.

(2) On the basis of the thermal stability and the vibration frequency related to the number of hydrogen atoms involved in these IR peaks, we attribute the 2210 cm^{-1} , 2066 cm^{-1} , 1980 cm^{-1} and 1832 cm^{-1} peaks to V + 4H, V + 3H, V + 2H and V + 1H defect complexes, respectively. A summary of the assignment, configuration and vibration modes corresponding to these IR peaks is listed in table 3.

(3) In the low-neutron-radiation-dose region, the formation of the V + 3H, V + 2H and V + 1H defect complexes results from the new radiation-induced defect complexes, in which hydrogen comes from dissolved hydrogen molecules in the c-Si and is IR inactive while, under the high-dose radiation, the V + 4H transforms into the V + 3H, V + 2H and V + 1H defect complexes.

Acknowledgments

We would like to acknowledge Professor Z L Wu for his guidance and encouragement during this work. We are also indebted to Professor T S Shi, Professor G R Bai and Mr P X Cai for discussions and help with this work.

References

- [1] Stein H J 1975 *J. Electron. Mater.* **4** 159
- [2] Cui S F, Ge P W, Zhao Y G and Wu L S 1979 *Acta Phys. Sin.* **28** 791 (in Chinese)
- [3] Zhang Z N and Xu Z J 1982 *Acta Phys. Sin.* **3** 994 (in Chinese)
- [4] Cui S F, Mai Z H and Tsien L C 1984 *Sci. Sin. A* **27** 213
- [5] Zhang Y F, Du Y C, Weng S F, Meng X T and Zhang B Z 1985 *Acta Phys. Sin.* **34** 849 (in Chinese)
- [6] Qi M W, Bai G R, Shi T S and Xie L M 1985 *Mater. Lett.* **3** 467
- [7] Bai G R, Qi M W, Xie L M and Shi T S 1985 *Solid State Commun.* **56** 277
- [8] Du Y C, Zhang Y F and Qin G G 1984 *Acta Phys. Sin.* **33** 477 (in Chinese)
- [9] Shi T S, Xie L M, Bai G R and Qi M W 1985 *Phys. Status Solidi b* **131** 511
- [10] Qi M W, Shi T S, Bai G R and Xie L M 1989 *Chin. J. Infrared Micrometer Waves* **6** 467
- [11] Bai G R, Zhou J K, Chen J M, Shi T S, Qi M W and Xie L M 1988 *Sci. Sin. A* **31** 499
- [12] Bai G R, Zhou J K, Chen J M, Shi T S, Qi M W and Xie L M 1988 *Sci. Sin. A* **31** 630
- [13] Chen J M, Xie L M, Bai G R and Zhao Y G 1989 *Phys. Status Solidi b* **153** 107
- [14] Chen J M, Xie L M, Bai G R and Zhou J K 1990 *Sci. Sin. A* **33** 1270
- [15] Wherrett B S 1986 *Group Theory for Atoms, Molecules and Solids* (Englewood Cliffs, NJ: Prentice Hall) p 53
- [16] Shi T S, Bai G R, Qi M W and Zhou J K 1986 *Mater. Sci. Forum* **10–12** 597
- [17] Du Y C, Zhang Y F, Meng X T and Sheng H Y 1987 *Sci. Sin. A* **30** 176 (in Chinese)
- [18] Mukashev B N, Nussryro K N, Tamendarov M F and Crolov V V 1982 *Phys. Lett.* **87A** 376
- [19] Qi M W, Shi T S, Zhao Y G, Cai P X and Gao J J 1989 *Radiat. Eff. Defects Solids* **111–2** 375
- [20] Shi T S, Sahu S N, Corbett J W and Snyder L C 1984 *Sci. Sin. A* **27** 98 (in Chinese)